

Gold nanoparticle synthesis in graft copolymer micelles

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Abstract An amphiphilic poly(acrylic acid)/polystyrene graft copolymer (PAA-g-PS) has been used to form “nanoreactors” for the synthesis of gold clusters. Such copolymers tend to form stable micelles in non-polar organic solvents where the poly(acrylic acid) chains constitute the core, and the polystyrene chains, the shell. In the present study, the micellar structure of PAA-g-PS in toluene has been demonstrated by dynamic light scattering and transmission electron microscopy (TEM).

The subsequent preparation of gold-graft copolymer composites involved the introduction of gold chloride (AuCl_3), either in powder form or previously dissolved in ether, into the micellar cores of the PAA-g-PS in toluene. The gold salt was then

reduced by ultraviolet (UV) irradiation of the emulsion, or of dried cast films. TEM and ultraviolet-visible (UV/Vis) spectroscopy were used to characterize the resulting composites. Gold particles of less than 5 nm in diameter were observed in all cases, but the size distribution and the spatial arrangement of the clusters in the cast films were modified when diethyl ether was used to introduce AuCl_3 into the PAA-g-PS micellar cores. This was thought to be due to enhanced nucleation of the gold particles and partial disruption of the micellar cores in the presence of diethyl ether.

Key words Gold clusters – graft copolymer – nanocomposites – optical properties – TEM

Introduction

Nanosized metal and semiconductor particles have recently attracted considerable interest owing to their potential in applications which exploit the non-linear optical and electronic properties arising from the size dependence of the band gap [1–3]. Such particles can be synthesized using physical methods [4] but have a strong tendency to agglomerate owing to their large specific surface area [5]. Various synthetic methods have therefore been developed in order to control and stabilize the particle size [6]. Organized superlattices of nanoparticles may also be

formed in which the particle spacing is determined by the nature of the ligands or stabilizer shells [7–9].

Methods using low molecular weight ligands are unsuitable for the formation of free-standing films. However, polymers may be employed as steric stabilizers and also as a means of controlling nanoparticle growth and interparticle spacing [10]. The resulting composites combine the optical and electrical properties of the particles and the cohesion and flexibility of the polymer. Diblock copolymers, which form a variety of morphologies by self-assembly, are a particularly attractive means of controlling nanoparticle dispersions. Ligand units may be selectively introduced into one of the blocks, and metals, such as

silver or gold, subsequently attached by complexation [11, 12]. Solvent evaporation and reduction of the metal-polymer complexes lead to the formation of isolated silver or gold clusters with diameters in the 3 nm range [13].

As well as undergoing self-organization in the bulk, diblock copolymers may form micelles in solution [14–16]. Such micelles can also serve as nanoreactors for the precipitation of inorganic clusters, provided that thermal motion is limited, so that the particle size and the interparticle separation can be controlled [17]. A high degree of control has been achieved in ordered micellar block copolymers, for example, with exactly one metallic particle per micelle being observed in cast films, with particle diameters down to 3 nm [18]. However, the inherent loss of entropy on precipitation of the solid particles in the micelles renders the stability poor and the block copolymers tend to re-organize into new stable micellar domains without particles at their centers. It has therefore been shown to be important to inhibit this process by rapid particle precipitation [19].

To investigate further the possibilities offered by micellar structures for the precipitation of gold nanoparticles, we have used micelles of an amphiphilic graft copolymer of poly(acrylic acid)/polystyrene (PAA-g-PS), since graft copolymers are expected to lead to thermodynamically more stable structures than block copolymers. When PAA-g-PS is introduced to a non-polar organic solvent, the micellar core is formed from the PAA backbone of the copolymer, and the shell is made up of the PS side-chains. A metal precursor, AuCl_3 may then be introduced into the micellar cores. A homogeneous dispersion of gold particles is anticipated on subsequent reduction, with the gold cluster growth being confined to the graft copolymer micellar cores, and the interparticle distance being determined by the effective size of the micelles.

Experimental

Materials

The solvents used for the anionic polymerization were purified using conventional procedures. Toluene was dried by refluxing in the presence of benzophenone-sodium complex under nitrogen. Diethyl ether was distilled from calcium hydride, AuCl_3 (Aldrich, 99.99%) was used as received.

Synthesis of graft copolymers

A more detailed description of the synthesis has been given previously [20]. Briefly, amphiphilic graft copolymers

were prepared via the macromonomer method, which consists of first preparing the side chains and then synthesizing the grafted structure by addition of the backbone monomer and the polymerizable terminal group at the branch ends.

Macromonomers were prepared by anionic polymerization of styrene in a mixture of cyclohexane and tetrahydrofuran (THF) (40/60) with *sec*-butyllithium slowly being added to the mixture. After 1 h of reaction, the polystyryllithium solution was transferred to another flask containing excess vinyl benzyl chloride in THF.

Free-radical copolymerization of the (vinylbenzyl) polystyrene macromonomer and acrylic acid (AA) was carried out in DMF in sealed tubes under argon at 60 °C initiated by azo-isobutyronitrile (AIBN). The copolymers were precipitated in methanol and extracted in diethyl ether or hot cyclohexane (50 °C) for several hours to remove any unreacted macromonomer.

Preparation of gold-graft copolymer suspensions and films

Inverse micelles of the copolymers were formed by dissolving 10 mg of copolymer in freshly distilled toluene (2 ml), and stirring for 48 h. To investigate the micellar structure of the copolymers in the suspensions, dynamic light scattering studies were carried out. A Coherent Innova 3000 krypton ion laser at a wavelength of 520.8 nm and a laser power of 40 mW was used as the light source. The scattered light was measured with a photomultiplier and the autocorrelation function was generated in real time with a Brookhaven Instrument correlator (B12030AT). The scattering angles were 60° and 90°. A refractive index matching bath of filtered toluene surrounded the scattering cell and the temperature was maintained at 25 °C. Typical concentrations for the dynamic light scattering measurements were 5 mg/ml. Averages were taken of five measurements made at each angle. To eliminate dust from the samples, stock solutions were filtered, and filtered toluene was used for dilution.

Two methods were used to add AuCl_3 (0.1 mol Au^{3+} per mole AA) to the copolymer micelles. The first method consisted of dissolving the AuCl_3 in diethylether (1 mg/ml) prior to mixing with the copolymer suspension in toluene. In the second method, the AuCl_3 was added directly to the suspension, which was subsequently stirred for several hours in order to promote dissolution of the salt in the copolymer micelles. Ultrathin films were obtained by spreading drops of the suspension onto a glass slide and slowly evaporating the solvent. The gold salt was then reduced using UV-Vis irradiation for 5–24 h at 45 °C in an accelerated exposure machine (Suntest) equipped with a Xenon lamp (NXe 1500, Atlas).

UV-Vis absorption spectroscopy

UV-Vis absorption spectra were recorded using a Perkin-Elmer Lambda 6 spectrophotometer at wavelengths between 190 and 800 nm. The solutions were analyzed in quartz cells, and solid films of about 100 μm in thickness were analyzed as cast onto non-absorbing glass slides.

Transmission electron microscopy (TEM)

A Philips EM430 ST at 300 kV (2 Å point to point resolution) was used for high-resolution transmission electron microscopy (HRTEM) and conventional TEM. Samples were prepared by placing a small drop of the micellar suspension either directly onto a carbon coated grid, or onto carbon coated mica (from which it was subsequently floated onto a copper grid using distilled water).

Lattice images were generally obtained at a magnification of 500 000 \times and at relatively strong underfocus (in order to optimize the contrast), leading to contrast reversal, i.e. columns of gold atoms appeared lighter than the background. No attempt was made to avoid beam damage of the polymer, and about 30 s of irradiation was necessary to crosslink and stabilize the matrix residue prior to observation. Even so it was necessary to avoid excessive beam intensities, which led to rapid recrystallization of the structures initially observed in the gold particles. Detailed observation of sub-nanometer sized particles was particularly difficult owing to their poor contrast against the organic background, their instability in the beam and to Brownian motion and/or drift.

Results and discussion

Micelle formation and characterization

Scheme 1 depicts the reaction path for the preparation of the PAA-g-PS copolymers. Data for copolymers obtained

using different amounts of macromonomer are summarized in Table 1. The characterization of the different copolymers has been detailed in an earlier report, in which the ability of the (PAA-g-PS) copolymers to form stable micelles in selective solvents was demonstrated by ^1H NMR spectroscopy [20]. It was shown that in organic solvents such as chloroform or toluene, inverse micelles are formed, such that the PAA backbone constitutes the solid core of the micelle, and the shell is composed of the dissolved polystyrene (PS) branches. PAA-g-PS is an example of a graft ionomer (an ionic graft copolymer), which shows particularly strong driving forces for micelle formation [21]. The concentration for the formation of multiple chain micelles in this type of copolymer is also very low.

The hydrodynamic diameters (D_h) for two PAA-g-PS copolymers (PAA-g-PS42 and PAA-g-PS41) in toluene have been determined by dynamic light scattering using the Rayleigh equations. The results (Table 1) were reproducible and diameters of 12 and 35 nm were obtained for PAA-g-PS42 and PAA-g-PS41, respectively. D_h for copolymer micelles is expected to be dependent on the length of the soluble block, the polarity of the solvent and the aggregation number. The copolymers used here had a fixed PS branch length so that the difference in D_h between the two copolymers was attributed to a greater degree of aggregation of the poly(acrylic acid) chains in PAA-g-PS41. The core of sample PAA-g-PS42 was also smaller owing to the lower PAA content. This was reflected by an observed decrease in the total scattering.

Micelle formation was also demonstrated by direct observation using TEM. A suspension of PAA-g-PS42 in toluene was treated with lead acetate ($\text{Pb}(\text{Ac})_3$) in order to stain the PAA core of the micelles. A drop of the stained micellar suspension was spread on a carbon substrate and dried. TEM micrographs (Fig. 1) showed dark domains with a diameter of about 2 nm, which is in the size range expected for the PAA core of the micelles. The distance

Scheme 1 Amphiphilic graft copolymer synthesis

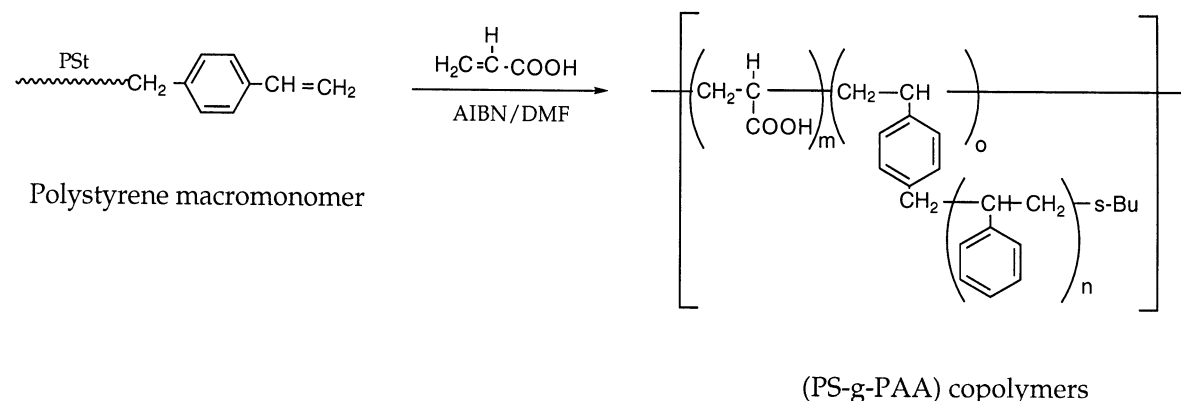


Table 1 Characteristics of PSt macromonomers copolymerized with acrylic acid

Run	PSt macromonomer		PSt in feed		PSt in copolymer		Copolymer	
	M_n	M_w/M_n	wt%	mol%	wt%	mol%	M_n	Micelle D_h [nm]
G-42	3500	1.05	70	4.6	65	3.5	31 000	12
G-41	3500	1.05	50	2	49	1.8	42 000	35

**Fig. 1** TEM micrograph of PS-g-PAA micelles stained with $Pb(Ac)_3$ and cast from toluene

between the micelles was about 10 nm, which is also consistent with the hydrodynamic diameter obtained by dynamic light scattering.

In situ reduction of gold

Scheme 2 summarizes the synthesis of gold nanosized particles, using the graft copolymer micelles as confined reactors. Solid gold chloride was either introduced directly into solutions of the graft copolymers in toluene, which is a poor solvent for the gold salt, or first dissolved in diethyl ether and then added to the solution. Both copolymers (PAA-g-PS41 and PAA-g-PS42) have been used for the synthesis. The salt remained dissolved in the mixed sol-

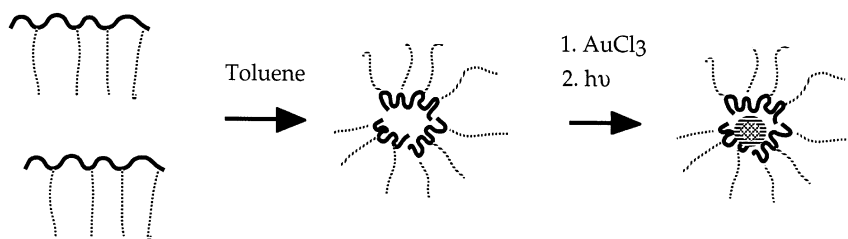
vent, however, it took several hours of stirring with the toluene mixture before homogenous clear yellow solutions were obtained.

Reduction of the gold chloride to gold metal was performed by UV irradiation either directly in solution or on cast films. UV irradiation has the advantage of not provoking reactions with the polymer, as might a chemical reducing agent, and it has already shown promise as a means of producing monodisperse gold particles [22].

Reduction was particularly rapid in the presence of diethyl ether, which may both act as an oxidizing agent and swell the poly(acrylic acid) core, increasing the molecular mobility and hence the reaction rate. While the reduction in solution occurred within a maximum of 5 h, cast films required up to 24 h UV exposure, owing to the restricted molecular mobility of the main chain poly(acrylic acid).

Particle characterization by TEM

TEM micrographs of particles formed with and without diethyl ether, using PAA-g-PS42 are shown in Fig. 2A and B, respectively. Histograms representing the approximate size distribution of the particles were obtained by digital analysis of images containing at least 200 particles (Fig. 3). The distribution of the particle diameters obtained with diethyl ether showed a main peak located between 1 and 1.5 nm. However, when toluene was the only solvent, diameter corresponding to the main peak diameter was greater (around 3 nm) and the size distribution somewhat broader and markedly bimodal with a second pronounced

Scheme 2 Formation of PS-g-PAA micelles in toluene and subsequent synthesis of gold nanoparticles

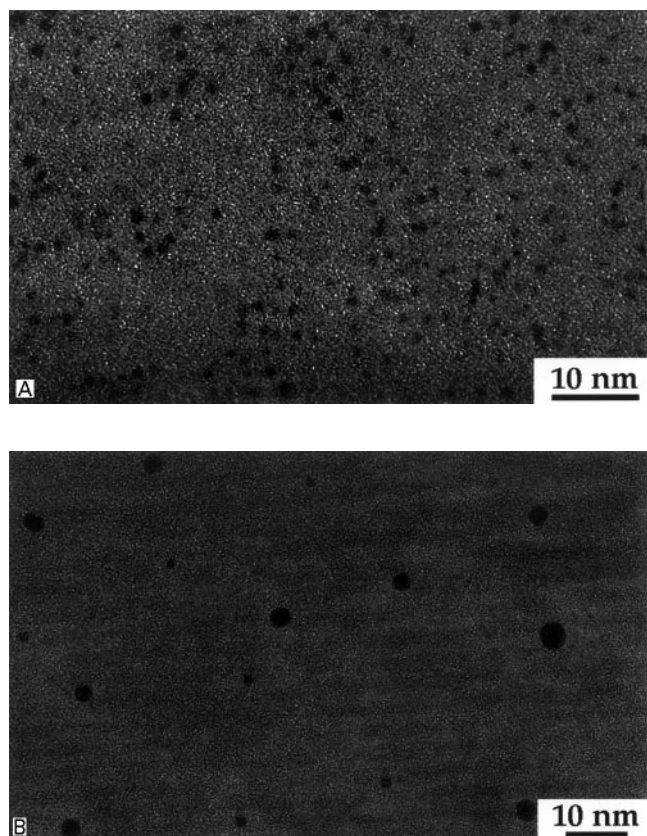


Fig. 2 TEM micrograph of gold particles produced by (A) photoreduction of AuCl_3 introduced in diethylether solution into the copolymer micelles in toluene and (B) by photoreduction of AuCl_3 introduced directly into the copolymer micelles in toluene

peak between 1 and 1.5 nm. Peaks in this latter range may correspond to the preferential formation of Au_{55} clusters, which have a diameter of 1.44 nm [23].

As stated earlier, reduction was accelerated by the presence of ether and particle nucleation was therefore assumed to be rapid, which accounts for the relatively narrow size distribution in this case. In the presence of toluene alone, for which the rate of reduction was lower, the broadening of the size distribution may be linked to a wider range of nucleation times.

It is also apparent from Fig. 2 that a less uniform and locally reduced interparticle spacing resulted from the presence of diethyl ether. This may be due to distortion of the micelles owing to swelling of the cores and multiple nucleations within individual micelles. Coalescence was, nevertheless, presumably prevented by the strong interactions between the growing particles and the carboxylic groups of the PAA. When toluene was the only solvent, one particle was thought to be associated with each individual micelle, so that the particle separation was determined by the micellar size which in this case was 12 nm.

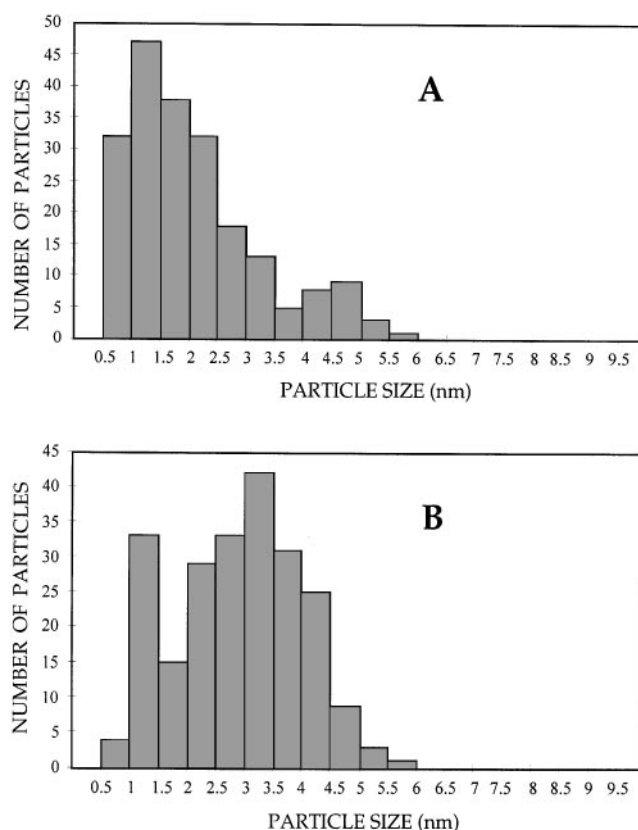


Fig. 3 Particle size distribution of gold particles produced by (A) photoreduction of AuCl_3 introduced in diethylether solution into the copolymer micelles in toluene and (B) by photoreduction of AuCl_3 introduced directly into the copolymer micelles in toluene

The crystalline structure of the larger particles obtained by both methods was clearly consistent with the face-centered cubic close packed structure of bulk gold. Images of appropriately oriented particles also frequently displayed fivefold twinning as shown in Fig. 4, which is thought to result from repeated tetrahedral capping of a tetrahedral nucleus (consisting of four gold atoms) during the initial stage of growth [5].

The image of the smaller particle in Fig. 4 illustrates the difficulty of lattice imaging for particle diameters of the order of, or less than about 1 nm. Although a reasonable estimate could be made of the particle sizes, it was not clear whether the smallest particles displayed the decahedral structure implied by the nucleation and growth mechanism referred to above.

Optical properties: UV–Vis absorption spectra

The films as well as the solutions showed a strong, broad absorption band with a maximum at 569 nm (Fig. 5). The

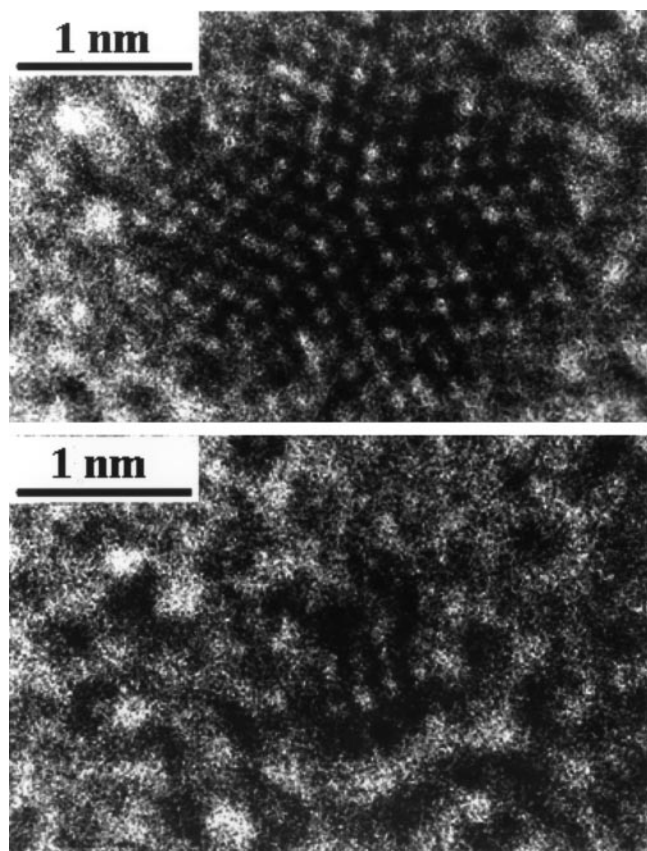


Fig. 4 High-resolution TEM micrographs of gold clusters produced by photoreduction of AuCl_3 introduced directly into the copolymer micelles in toluene

position and the shape of the band were very similar for the two methods of introduction of AuCl_3 into the solutions but differed significantly from those observed at 530–540 nm in the surface plasmon resonance spectrum of nanogold particles reported elsewhere [23].

Several explanations might be advanced to account for this red shift. For example, for large (diameter > 20 nm) or agglomerated particles (which were not observed), the retarded polarization produces light scattering and a red-shift of the extinction maximum. The absorption band of very small clusters (diameter < 2 nm) is also red shifted and broadened owing to size-dependent damping of the metal dielectric function. A further mechanism leading to a red shift is a reduction of electron density in the gold particles owing to chemical interactions with the surrounding poly(acrylic acid) ligands, favoring the transition of electrons from the cluster to the surrounding matrix. The red shift observed in the present case may be due to the combination of these last two effects.

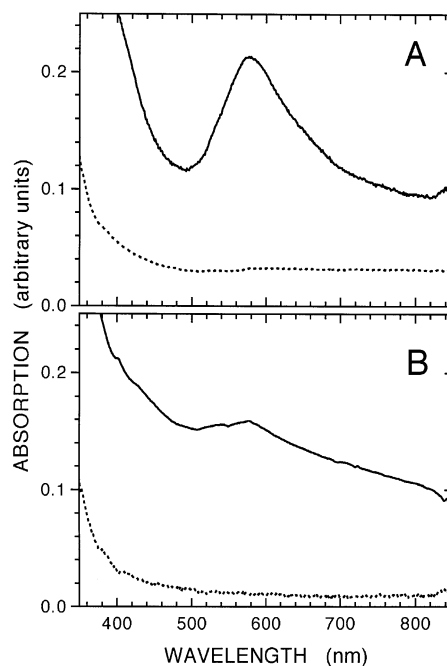


Fig. 5 Optical absorption spectra of films cast from micellar solutions containing AuCl_3 . Spectra were taken before (dotted lines) and after UV reduction (solid lines) from films prepared from solution with (A) and solution without diethylether (B)

Conclusions

Micellar domains which are formed when polystyrene-g-poly(acrylic acid) is mixed with toluene can serve as stable confined domains for the preparation of 1–5 nm diameter gold clusters by photoreduction. The PAA-rich cores of the micelles dissolve and contain the AuCl_3 , while the polystyrene branches surrounding the particles hinder the agglomeration and control the interparticle distance. Controlled three-dimensional packing of nanosized particles could therefore be achieved by self-organization of the stabilized clusters on casting from solution. The resulting polymer–Au cluster composites nevertheless exhibited a UV absorption at 570 nm which represents a substantial red shift with respect to the expected surface plasmon resonance at 530 nm.

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